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# The Origin of Surface Charges on the $\beta$ -CaSiO<sub>3</sub>/Dimethyl Sulfoxide Interface<sup>1</sup>

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The surface charge on  $\beta$ -CaSiO<sub>3</sub> in dimethyl sulfoxide is influenced to a large extent by alkali ions, which may be adsorbed from the surrounding liquid or desorbed from the solid when present as an impurity. Exchange of Na<sup>+</sup> by Ca<sup>2+</sup> is observed. Dissolution of silica from CaSiO<sub>3</sub> probably does not contribute to the surface charge. Br<sup>-</sup> ions, present in the liquid phase as counter ions for Na<sup>+</sup> and Ca<sup>2+</sup>, are only adsorbed to a measurable extent when the surface is positively charged. On the basis of an electrostatic model and assuming absence of complex formation between Ca<sup>2+</sup> and Br<sup>-</sup> in the solution, the potential is calculated Br<sup>-</sup> ions behind the electrokinetic slipping plane are on the average subject to. This potential decreases with  $\sigma_{Br^-}$  in CaBr<sub>2</sub> solutions, but increases again when appreciable amounts of Na<sup>+</sup> ions are present.

## INTRODUCTION

In aqueous media, H<sup>+</sup> and OH<sup>-</sup> ions play a dominant role in the determination of the surface charges on oxidic materials (1-10). Much less is known about the origin of surface charges of oxidic materials in aprotic media such as dimethyl sulfoxide (DMSO). It was thought worth while to compare in this medium the net surface charge found behind the electrokinetic slipping plane, with adsorption measurements of all species involved.

As solid phase,  $\beta$ -CaSiO<sub>3</sub> (wollastonite) was employed because it can be prepared with a reasonably large surface area (7-10 m<sup>2</sup> g<sup>-1</sup>) as required for adsorption measurements. Adsorption and desorption of Ca<sup>2+</sup> and silicate ions was studied because these ions make up the solid phase; Na<sup>+</sup>, added initially as an ion necessary to adjust the liquid medium to constant ionic strength on varying Ca<sup>2+</sup> concentration, appeared to be a dominant factor in determining the surface charge. As counter ion for Ca<sup>2+</sup>

and Na<sup>+</sup> in the liquid phase Br<sup>-</sup> was employed, because of ease of determination.

## EXPERIMENTAL

*Materials.*  $\beta$ -CaSiO<sub>3</sub> was prepared through the reaction sequence:

- (a)  $2 \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2 \text{CO}_2$ ,
- (b)  $3 \text{Ca}_2\text{SiO}_4 + 3 \text{SiO}_2 + \text{H}_2\text{O} \rightarrow 6 \text{CaO} \cdot 6 \text{SiO}_2 \cdot \text{H}_2\text{O}$  (xonotlite),
- (c)  $6 \text{CaO} \cdot 6 \text{SiO}_2 \cdot \text{H}_2\text{O} \rightarrow 6 \beta\text{-CaSiO}_3 + \text{H}_2\text{O}$ .

Reaction (a) comprised successive heatings at 1425°C (4 hr) and 1600°C (4 hr), reaction (b) treatment in an autoclave (220°C, 120 hr, water/solids ratio w:w = 1.5), reaction (c) heating at 950°C (2 × 7 hr, with intermittent grinding).

Two samples were used, one (high Na) from CaCO<sub>3</sub> (Merck, pro analysi) and quartz (Merck, <36  $\mu\text{m}$ ), with a Na content of 1400 ppm and an Areameter (Ströhlein) N<sub>2</sub> adsorption surface area of 7.0 m<sup>2</sup> g<sup>-1</sup>; the other (low Na) from CaCO<sub>3</sub> (Merck, Suprapur) and

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quartz, with a Na content of 28 ppm and an Areameter surface area of  $9.2 \text{ m}^2 \text{ g}^{-1}$ .

Dimethyl sulfoxide (Fluka, A. G.) was distilled *in vacuo* from  $\text{CaH}_2$  through a 0.75 m length column (boiling point  $40^\circ\text{C}$ ). Gas chromatographic analysis, using a column containing 10% PEG 600 on no. 100-mesh gc at  $80^\circ\text{C}$ , showed that organic impurities, originally present in the commercial DMSO, were almost completely removed. The water content (Karl Fischer titration) was  $< 300$  ppm.

$\text{CaBr}_2$  (Merck) was dried *in vacuo* ( $110^\circ\text{C}$ , 20 hr). The final  $\text{CaBr}_2$  content was found as 99.95% (based on Ca) and 99.65% (based on Br).

$\text{NaBr}$  (Merck) was recrystallized and dried *in vacuo* ( $110^\circ\text{C}$ , 7 hr).

*Methods.*  $\text{Ca}^{2+}$  was determined by complexometric photometric titration (11).  $\text{Br}^-$  was determined by potentiometric titration with  $\text{AgNO}_3$ , using a  $\text{Ag}/\text{AgBr}$  indicator electrode (12) and a mercurous sulphate reference electrode and an Orion digital pH measuring unit model 701. 3–8 ml of DMSO solution (depending on the concentrations) were diluted with water before titration to 100 ml; 25 ml of this solution + 10 ml ( $0.5 \text{ M KNO}_3 + 0.01 \text{ M HNO}_3$ ) solution were titrated in the dark.  $\text{AgNO}_3$  solution was added from a Metrohm E 437 0.5 ml microhandburette; after every addition, the EMF was read after waiting for 1 min. Titration was based on weight rather than volume; the endpoint was determined by Gran's method (13). The standard deviations in the equivalent volume according to linear regression applied on the Gran function as  $f$  (volume of titrant) was 0.7–1.5%, and usually exceeded that of triplo determinations (0.1–0.5%).

$\text{Na}^+$  in liquids was determined by adding known quantities of  $\text{Na}^+$  ions to the solution while following the EMF of a combined Na sensitive glass electrode (Philips C 15 Na) through a Corning-Eel Model 113 digital pH meter. The amount of  $\text{Na}^+$  containing solution was chosen such as to give, after dilution to 100 ml with buffer solution (5 parts 1  $\text{M}$  triethanolamine + 2 parts 1  $\text{M}$   $\text{HCl}$  + 2 parts

$\text{H}_2\text{O}$  (14)), an approximately  $4 \cdot 10^{-4} \text{ M}$  solution. The EMF as  $f$  (volume of  $\text{Na}^+$  solution of known concentration) was plotted after Gran (13). Standard deviations in equivalent volume during one titration generally fell between 0.2 and 0.5%, but differences between triple determinations sometimes exceeded this value.

$\text{Na}^+$  in solids was determined by neutron activation analysis. A 100 mg sample was irradiated in a neutron flux of  $10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$  during 1 hr. After 1–5 days of decay; counting of the 1.368 MeV peak of  $^{24}\text{Na}$  was performed by means of a  $30 \text{ cm}^3 \text{ Ge(Li)}$  semiconductor detector.

$\text{Na}^+$  was determined both in untreated  $\beta\text{-CaSiO}_3$  samples and in samples that had been subjected to adsorption measurements in  $\text{NaBr}$ -free solutions. In the latter cases, the wet samples were heated in Pt crucibles (final temperature  $600^\circ\text{C}$ ). The values were employed to calculate final  $\text{Na}^+$  concentrations in the liquid in the experiments without  $\text{NaBr}$  in the initial liquid phase.

Silica was determined photometrically after conversion to yellow silicomolybdic acid (15). Five milliliter samples of DMSO solutions were diluted to 25 ml with 0.01  $\text{M HCl}$ ; blanks during the determination of the optical density contained the same amounts of DMSO. Electrophoresis was carried out in a double-tube microelectrophoresis cell (16) consisting of Pyrex glass; in some cases, the values were checked by electroosmosis (17), giving (within  $\pm 10\%$ ) the same values. The  $\zeta$ -potential was calculated by the Smoluchowski equation (18) assuming  $\kappa a \gg 1$ . The particles (as seen in the electrophoresis cell) were conglomerates with diameter  $> 3 \mu\text{m}$ ; at the lowest ionic strength employed,  $\kappa a$  would be 110. According to Wiersema *cs* (19) deviations for a spherical particle from the Smoluchowski equation should not exceed 4%.

Adsorption experiments were performed on 2 g samples, suspended in DMSO solutions in 50 ml polythene vessels, keeping the solid/liquid ratio constant (e.g., w:w = 1:20) in a series. Contact time between solid and liquid

was at least 20 hr with at least 9 hr of shaking. Before analysis, the suspension was subjected to centrifugation ( $2 \times 30$  min at 8000 rpm).

Calculation of surface charges behind the electrokinetic slipping plane: The total surface charge behind the electrokinetic slipping plane was calculated from the  $\zeta$ -potential on the basis of the Gouy-Chapman theory (cf. (20, formula 2.31)).

The surface charge behind the electrokinetic slipping plane, due to one particular ionic species, was calculated from the amount of the species concerned that was adsorbed, diminished by the amount present in the diffuse double layer as calculated again from the Gouy-Chapman theory by means of the formula:

$$\sigma_i = z_i e_0 \int_{\psi=\zeta}^0 \frac{N_{i\infty} [\exp(-z_i e_0 \psi / kT) - 1]}{d\psi/dx} d\psi,$$

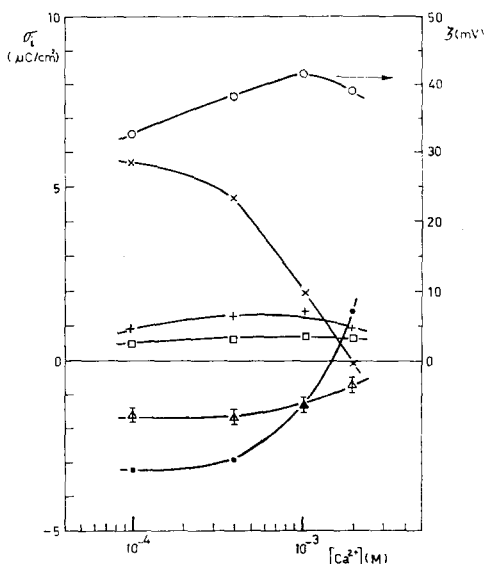
where  $N_{i\infty}$  = the bulk concentration (number per  $\text{cm}^3$ ) of the species concerned in the liquid;  $z_i$  = its valency (sign included),  $e_0$  = the charge of a proton (C).

If  $d\psi/dx$  is expressed in  $V \text{ cm}^{-1}$ ,  $\sigma$  is obtained in  $C \text{ cm}^{-2}$ . A flat double layer value for  $d\psi/dx$  was employed. At the smallest ionic strength employed ( $3 \times 10^{-4} M$ ),  $\kappa a$  would become about 8 ( $a$ : estimated from the surface area). The correction for a nonflat (spherical) double layer would then be about 10%; at higher concentrations, it would be lower. Since  $|\sigma_i|$  is much smaller than the surface charges calculated from the analyses, the correction was considered to be useless in connection with the analytical errors.

Silicate desorption was calculated initially to account for a surface charge amounting  $+2e_0$  per  $\text{SiO}_2$  unit desorbed; for a discussion of this assumption, see below.

## RESULTS

For the  $\beta$ - $\text{CaSiO}_3$  sample of low  $\text{Na}^+$  content (28 ppm), the  $\zeta$ -potential was invariably found to be positive at all concentrations of  $\text{NaBr}$  and  $\text{CaBr}_2$  studied (Figs. 1-4). If the  $\beta$ - $\text{CaSiO}_3$  contains, however, relatively large amounts of



FIGS. 1-5. Charges  $\sigma_i$  ( $\mu\text{C}/\text{cm}^2$ ) behind  $\zeta$  plane: ●,  $\text{Ca}^{2+}$ ; ×,  $\text{Na}^+$ ; Δ,  $\text{Br}^-$ ; ⊕,  $\text{SiO}_3^{2-}$ ; □,  $|\sigma_d|$ , and  $\zeta$ -potential (○).

FIG. 1. Adsorption measurements on low Na  $\beta$ - $\text{CaSiO}_3$  at  $I \approx 0.006 M$  ( $\text{CaBr}_2 + \text{NaBr}$ ).

$\text{Na}^+$  (e.g., 1400 ppm), the  $\zeta$ -potential may be negative (Fig. 5). In these cases, no  $\text{Br}^-$  adsorption was detected, even if the absolute value of  $\zeta$  was quite low. For instance: In the experiment with  $\zeta = -8.3$  mV, the measured  $\text{Br}^-$  concentration was  $5.438 \times 10^{-3} M$  with reference to the original concentration  $5.432 \times 10^{-3} M$ . The probable error of the difference was  $0.010 \times 10^{-3} M$ .

For the high Na content  $\text{CaSiO}_3$ , it follows from the adsorption and desorption measurements that in this case, the negative charge behind the electrokinetic slipping plane is due to  $\text{Na}^+$  desorption from the solid, which is only partly compensated by  $\text{Ca}^{2+}$  adsorption; the contribution of desorption of part of the silicate anion skeleton is small compared with  $\sigma_{\text{Na}^+}$  and  $\sigma_{\text{Ca}^{2+}}$ . The desorption of  $\text{Na}^+$  increases with increasing  $\text{Ca}^{2+}$  concentrations at constant ionic strength in the surrounding liquid (Fig. 5); this can be interpreted as an exchange of  $\text{Na}^+$  by  $\text{Ca}^{2+}$  in surface sites.

Similar observations are made on low Na content  $\text{CaSiO}_3$ . Here  $\sigma_{\text{Na}^+}$  and  $\sigma_{\text{Ca}^{2+}}$  have

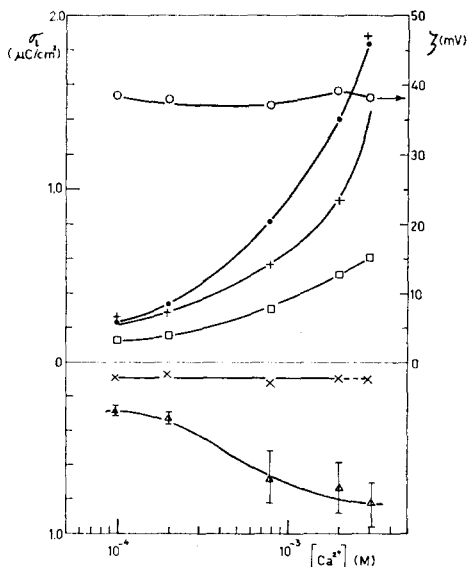


FIG. 2. Adsorption measurements on low Na  $\beta$ -CaSiO<sub>3</sub> in pure CaBr<sub>2</sub> solutions.

opposite sign;  $\sigma_{Na^+}$  becomes negative at low Na<sup>+</sup> concentrations in the surrounding liquid, but at higher Na<sup>+</sup> concentrations,  $\sigma_{Na^+}$  is positive, and  $\sigma_{Ca^{2+}}$  is negative even at rather high Ca<sup>2+</sup> concentrations. Again, this can be

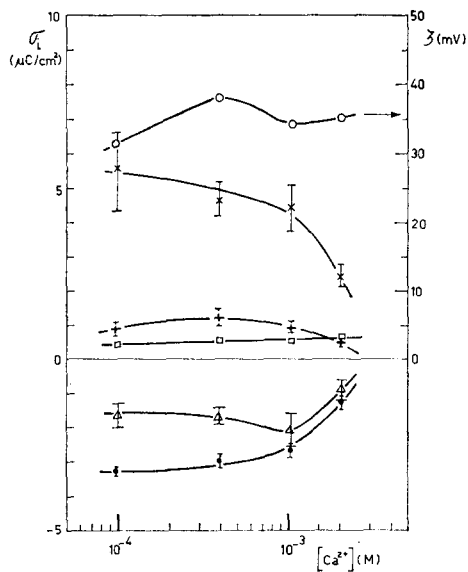


FIG. 3. Adsorption measurements on low Na  $\beta$ -CaSiO<sub>3</sub> at nearly constant NaBr concentration ( $6 \times 10^{-3} M$ ) and varying CaBr<sub>2</sub> concentration.

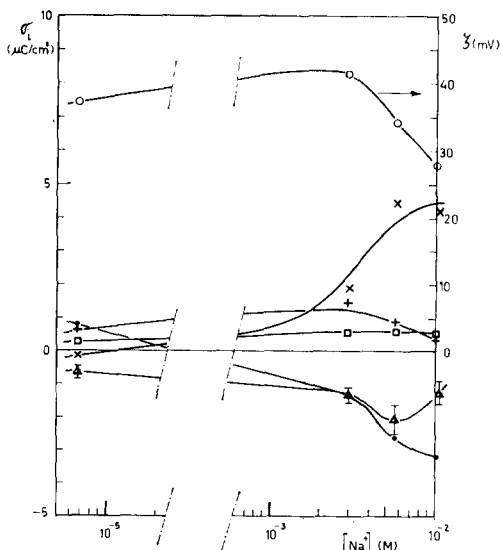


FIG. 4. Adsorption measurements on low Na  $\beta$ -CaSiO<sub>3</sub> at nearly constant CaBr<sub>2</sub> concentration ( $10^{-3} M$ ) and varying NaBr concentration.

interpreted as an exchange of Ca<sup>2+</sup> by Na<sup>+</sup> in surface sites.

In Figs. 1-4, the standard deviations of  $\sigma_{Br^-}$  are shown, in Fig. 3, those of all  $\sigma_i$ .

In Fig. 3 and Fig. 4,  $|\sigma_{Br^-}|$  at the highest Ca<sup>2+</sup>, respectively, Na<sup>+</sup> concentration used is considerably lower than at somewhat lower concentrations. This effect was also found in

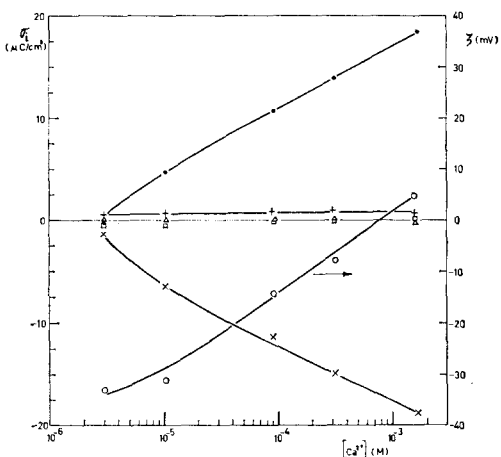


FIG. 5. Adsorption measurements on "high" Na  $\beta$ -CaSiO<sub>3</sub> at  $I \approx 0.006 M$  (CaBr<sub>2</sub> + NaBr).

experiments with a second  $\beta$ -CaSiO<sub>3</sub> sample of low Na<sup>+</sup> content.

It cannot be attributed to ionic or organic impurities in the NaBr- and CaBr<sub>2</sub>-stock solutions, because it was only observed with combinations of high CaBr<sub>2</sub> and NaBr concentrations ( $a_{\text{Br}^-} > 7 \times 10^{-3} M$ ), not in solutions containing CaBr<sub>2</sub> only (up to  $4 \times 10^{-3} M$ ).

By gas chromatography, no organic impurities could be detected in the stock solutions kept in glass vessels after 3 months of standing, or in solutions kept in polythene vessels in contact with solid  $\beta$ -CaSiO<sub>3</sub> for periods up to 1 month.

### DISCUSSION

The results demonstrate the great influence of low impurity (Na<sup>+</sup>) concentrations on the surface charge density acquired by the suspended sample. As yet, no data are available about the state in which the sodium is present. According to Moir and Glasser (21) Na<sub>2</sub>SiO<sub>3</sub> is not soluble in  $\beta$ -CaSiO<sub>3</sub>, but a binary phase Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> with a varying stoichiometry exists. The sodium concentration present in our samples is, however, too small (<0.2 mole%) to exclude its homogeneous dispersion in the  $\beta$ -CaSiO<sub>3</sub>. It is improbable that sodium ions present in a separate phase could influence the  $\zeta$ -potential to the extent observed.

Especially interesting from a colloid chemical point of view is the adsorption of Br<sup>-</sup> on a positively charged  $\beta$ -CaSiO<sub>3</sub> surface, because of the absence of specific adsorption on a negatively charged surface. In aqueous media, absence of specific adsorption of Cl<sup>-</sup> on oxides and silicates has been shown repeatedly (4, 7, 22, 23); in DMSO some arguments for the absence of specific adsorption of I<sup>-</sup> on silicates have been presented (24).

Adsorption on a positively charged surface may serve then as a test of the various theoretical models.

A simple electrostatic model, treating all adsorbed Br<sup>-</sup> ions as being present in a diffuse double layer (25) and identifying the potential of ions that approach the solid most closely with the potential in the outer Helmholtz

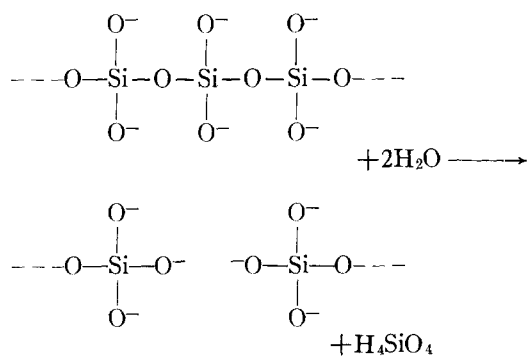
plane  $\psi_0$ , yields large values for the distance between oHp and electrokinetic slipping plane varying from 14 Å (ionic strength  $1.2 \times 10^{-2} M$ ) to 120 Å (ionic strength  $3 \times 10^{-4} M$ );  $\psi_0$  thus calculated consistently surpasses  $\zeta$ . Such an increase in distance between oHp and electrokinetic slipping plane with decreasing ionic strength cannot be explained through a viscoelectric effect (cf. Li and de Bruyn (25)) since this would act exactly in the opposite direction. Neither can a correction for a nonflat (spherical) double layer explain the effect: this results in the distances mentioned becoming somewhat smaller (120 Å, for instance, becoming 105 Å). This simple electrostatic theory, obviously, cannot account for the adsorption of the Br<sup>-</sup> ions. We conclude that part of the Br<sup>-</sup> ions disappearing from the solution, is taken up into the Stern layer. As simplest assumption the electrokinetic slipping plane is thought here to coincide with the oHp.

In Fig. 6,  $|\sigma_{\text{Br}^-}|$  is plotted as a function of  $\sigma_0$ , the charge on the solid per unit area. In this figure, the probable error shown is due to the uncertainty in  $\sigma_{\text{Br}^-}$  rather than in  $\sigma_d$ . Table I gives a survey of data on low Na  $\beta$ -CaSiO<sub>3</sub>.  $\sigma_0$  has been calculated here as  $-\sigma_d - \sigma_{\text{Br}^-}$  (where  $\sigma_d$  = total charge per unit area in the diffuse double layer). The use of this formula implies that other charges behind the electrokinetic slipping plane, except  $\sigma_{\text{Br}^-}$ , are thought to be located on the solid. Indeed,  $\sigma_{\text{Ca}^{2+}}$  may always safely be thought to be located on the solid since Ca<sup>2+</sup> ions fit well into the solid phase, and are strongly repelled from the interface in the direct vicinity of a positively charged surface. The  $\sigma_{\text{Na}^+}$  is certainly located on the solid when  $\sigma_{\text{Na}^+}$  is negative, as in the experiments with low NaBr concentrations ( $< 10^{-5} M$ ).

At higher NaBr concentrations, however, some Na<sup>+</sup> present behind the electrokinetic slipping plane may be located between the Br<sup>-</sup> ions in the inner Helmholtz plane, in spite of the positive average potential in this plane. This is supported by the following facts: In Fig. 6,  $d|\sigma_{\text{Br}^-}|/d\sigma_0$  decreases with increasing

$\sigma_0$  as long as there are only minor amounts ( $<10^{-5} M$ ) of NaBr present in the solution; but in the presence of appreciable amounts of NaBr ( $>10^{-3} M$ )  $d|\sigma_{Br^-}|/d\sigma_0$  has a nearly constant, larger value than in NaBr-free solutions. This suggests that part at least of a positive  $\sigma_{Na^+}$  should be thought to be located not on the solid, but between the  $Br^-$  ions in the space between the solid and the electrokinetic slipping plane, screening off electrostatic repulsion between the  $Br^-$  ions. At low NaBr concentration,  $Ca^{2+}$  ions screen off the repulsion between adsorbed  $Br^-$  ions to a minor extent because they are repelled more strongly from the iHp by a positive surface charge than  $Na^+$  ions. If this interpretation is right, then  $\sigma_0$  for the experiments with high NaBr concentrations as plotted in Fig. 6 is too high, since part of  $\sigma_{Na^+}$  should be subtracted from it and the points concerned should be shifted to the left.

It is questionable, whether  $\sigma_0$  should be considered to comprise a contribution from the dissolution of silica. If this process consists simply of a breaking off of  $SiO_3^{2-}$  ions from the  $[SiO_3]_{\infty}$  chains in the wollastonite structure (26), every dissolved  $SiO_2$  unit leaves behind two positive unit charges. However, the  $SiO_2$  found analytically in DMSO may be present there in an unionized form (cf. the fact that amorphous silica, aerosil, dissolves easily in DMSO, forming a clear solution). In this case, the dissolution of silica from wollastonite might comprise a reaction with traces of water, such as:



The  $\sigma_{SiO_3^{2-}}$  would then be zero. A similar result

would be obtained if  $SiO_3^{2-}$  ions dissolving from the  $CaSiO_3$  would react in solution with water, forming  $H_4SiO_4 + 2 OH^-$ , with the  $OH^-$  ions subsequently being adsorbed by the  $CaSiO_3$ .

A comparison of  $\sigma_0 = -\sigma_d - \sigma_{Br^-}$  with analytically determined values of  $\sigma_{Ca^{2+}}$ ,  $\sigma_{Na^+}$ , and " $\sigma_{SiO_3^{2-}}$ " shows a better agreement of  $\sigma_0$  with  $\sigma_{Ca^{2+}} + \sigma_{Na^+}$  than with  $\sigma_{Ca^{2+}} + \sigma_{Na^+} + \sigma_{SiO_3^{2-}}$ .

In addition, for the bulk solution the condition  $\sum_i c_i z_i = 0$  ( $c_i$  = concentration of ionic species  $i$ ,  $z_i$  = its valency, sign included) is fulfilled better when the silica found in the solution is being regarded as being uncharged.

However,  $\sum_i c_i z_i$  falls within the experimental error of the determinations of the ionic species that are present in large concentrations.

We calculated from  $\sigma_{Br^-}$  the potential  $\psi_{\beta}^1$  corresponding with a standard free enthalpy of adsorption, applying for the  $Br^-$  ions behind the electrokinetic slipping plane the equation (27):

$$\begin{aligned}
 \frac{\sigma_{Br^-}}{nf} &= \frac{(N_s z_{Br^-} e_0 - p \sigma_{Br^-})^p}{n_0 (N_s z_{Br^-} e_0)^{p-1}} \\
 &\quad \times \exp(-z_{Br^-} e_0 \psi_{\beta}^1 / kT),
 \end{aligned}$$

where

$$\psi_{\beta}^1 = \frac{\Phi}{-z_{Br^-} e_0} + \psi_{\beta} + \varphi_{\beta}''$$

with:  $\Phi$  = the real specific adsorption energy of the  $Br^-$  ion;  $\psi_{\beta}$  = mean electrostatic potential in the iHp;  $\varphi_{\beta}''$  = self-atmosphere potential;  $n$  = number of  $Br^-$  per unit volume in the bulk liquid;  $n_0$  = number of DMSO molecules per unit volume in the bulk liquid;  $z_{Br^-} = -1$ ;  $f$  = activity coefficient of  $Br^-$ ;  $N_s$  = number of sites for (unsolvated)  $Br^-$  ions per unit area;  $p$  = number of adsorption sites occupied (on the average) by an adsorbed  $Br^-$  ion;  $p$  may be  $>1$  for a solvated  $Br^-$  ion; and  $f$  was calculated from the Debye-Hückel theory assuming absence of complex formation between  $Ca^{2+}$  and  $Br^-$  ions in the solution (as suggested by the absence of specific adsorption of  $Br^-$  on  $CaSiO_3$  when negative, compare Lohmann (28)).

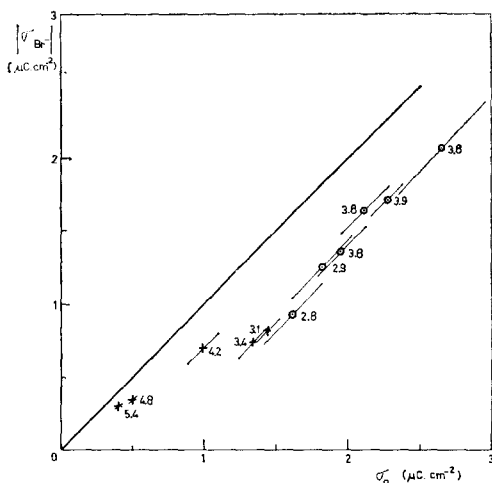


FIG. 6. Adsorption measurements on low Na  $\beta$ -CaSiO<sub>3</sub>. Plot of  $\sigma_{Br^-}$  versus  $\sigma_0$  (charge on the solid per unit area): +, solutions with low Na<sup>+</sup> concentration ( $<10^{-5} M$ ); O, solutions with high Na<sup>+</sup> concentration ( $>10^{-5} M$ ). The numbers besides the symbols are the values of  $\psi_{\beta}^1$  (in units  $kT/e_0$ ).

The resulting  $\psi_{\beta}^1$  is to some extent, but not strongly, dependent on the values for the parameters  $N_s$  and  $p$  employed. For  $p = 1$  and  $N_s = 6.5 \times 10^{14} \text{ cm}^{-2}$  (which applies if the Br<sup>-</sup> ions behind the electrokinetic slipping plane are situated in one inner Helmholtz plane),  $\psi_{\beta}^1$  is shown in units  $kT/e_0$  in Fig. 6. In agreement with the explanation given,  $\psi_{\beta}^1$  decreases with increasing  $|\sigma_{Br^-}|$  as long as [NaBr] remains small (mutual repulsion

between Br<sup>-</sup> ions in the inner Helmholtz plane) but increases again when there are present high concentrations of NaBr in the surrounding liquid. Since both  $|\sigma_{Ca^{2+}}|$  and  $|\sigma_{Na^+}|$  remain small (when the exchange of Ca<sup>2+</sup> by Na<sup>+</sup> is at its maximum a few percent of all surface sites are occupied by Na<sup>+</sup>), it is improbable that a change in character of the CaSiO<sub>3</sub> surface itself might be responsible.

In spite of these variations in  $\psi_{\beta}^1$ , the  $\zeta$ -potential remains remarkably constant. This indicates that the variations in  $\psi_{\beta}^1$  are not caused by large variations in the mean potential ( $\psi_{\beta}$ ) in the plane concerned. It is natural to suppose that the potential on a solid insulator varies locally; therefore, the potential in the Stern layer will show local variations too. In the  $\zeta$ -potential on the other hand, these local variations are averaged out. Thus, the potential Br<sup>-</sup> ions in the Stern layer are on the average subject to, should be distinguished from the mean potential in the plane concerned. The decrease of  $\psi_{\beta}^1$  with increasing  $\sigma_0$  at low [NaBr] can then be ascribed partially to favourable positions becoming occupied.

It will be noticed that  $\sigma_0$  (calculated as  $-\sigma_d - \sigma_{Br^-}$ ) is rather low in solutions high in both [NaBr] and [CaBr<sub>2</sub>]. Since a high  $\sigma_0$  is due under these circumstances primarily to a strongly positive  $\sigma_{Na^+}$ , this effect has to be ascribed to a reduced tendency of Na<sup>+</sup> to

TABLE I  
Survey of Data on Low Na  $\beta$ -CaSiO<sub>3</sub>

[Ca <sup>2+</sup> ]	[Na <sup>+</sup> ]	$\sigma_{Br^-}$	$\sigma_{Ca^{2+}}$	$\sigma_{Na^+}$	$\sigma_{Br^-}$	" $\sigma_{SiO_2}$ "	$\sigma_d$	$\sigma_0$	$\zeta$	$\psi_{\beta}^1$	$y = \frac{\psi_{\beta}^1 e_0}{kT}$
$10^{-3} M$			$(\mu C \text{ cm}^{-2})$						(mV)	(mV)	
1.043	2.891	4.14	-1.32	+1.91	-1.36	+1.36	-0.593	+1.95	41.4	97	3.8
0.389	4.835	4.71	-2.98	+4.64	-1.71	+1.22	-0.564	+2.28	38.2	100	3.9
0.099	5.666	4.97	-3.28	+5.71	-1.64	+0.90	-0.478	+2.12	32.6	97	3.8
1.964	0.006	3.33	+1.41	-0.10	-0.74	+0.93	-0.507	+1.28	39.1	88	3.4
0.199	0.004	0.367	+0.33	-0.07	-0.34	+0.30	-0.157	+0.50	38.0	123	4.8
0.783	0.007	1.39	+0.80	-0.12	-0.69	+0.56	-0.303	+0.99	37.2	107	4.2
0.098	0.005	0.179	+0.22	-0.10	-0.30	+0.24	-0.118	+0.41	38.4	138	5.4
2.050	5.705	7.81	-1.29	+2.47	-0.92	+0.54	-0.695	+1.61	35.4	71	2.8
1.081	5.567	6.30	-2.63	+4.48	-2.06	+0.91	-0.591	+2.65	34.3	97	3.8
2.958	0.006	4.87	+1.90	-0.10	-0.83	+1.96	-0.599	+1.42	37.8	80	3.1
1.132	9.77	9.48	-3.17	+4.22	-1.24	+0.36	-0.588	+1.82	28.1	73	2.9



become adsorbed. Its ultimate reasons are at present not clear, but perhaps there is a connection with the low values of " $\sigma_{\text{SiO}_3^{2-}}$ " found in the experiments concerned.

### CONCLUSIONS

1.  $\text{Na}^+$  ions play an important role in the determination of the surface charge on  $\beta\text{-CaSiO}_3$  in dimethyl sulfoxide: When present in relatively large amounts in the solid phase, their desorption, which is only partly compensated by  $\text{Ca}^{2+}$  adsorption, produces a negative surface charge; when present in small amounts, their adsorption produces a positive surface charge.

2.  $\text{Br}^-$  adsorption requires an electrostatic attraction.

3. With increasing surface charges in solutions of low  $[\text{NaBr}] d|\sigma_{\text{Br}^-}|/d\sigma_0$  decreases; but it is higher again when appreciable concentrations of  $\text{NaBr}$  are present.

4. This is ascribed to screening off of the mutual electrostatic repulsion between  $\text{Br}^-$  ions in the iHp by  $\text{Na}^+$  ions between them, whereas  $\text{Ca}^{2+}$  ions have a tendency to be incorporated in the solid when present behind the electrokinetic slipping plane.

5. Dissolution of silica from  $\text{CaSiO}_3$  probably does not contribute to  $\sigma_0$ .

6. An electrostatic model treating all adsorbed  $\text{Br}^-$  ions as being present in a diffuse double layer does not hold.

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